ELECTROPHORETIC MOBILITY OF CONCENTRATED COAL SUSPENSIONS

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Abstract: A variety of properties of dry coal powders and of coal/water slurries have been measured for ten bituminous coals, some available as both ROM and beneficiated samples. Slurry rheology, maximum solids content and stability towards sedimentation are in general related to the electrophoretic mobility measured in concentrated suspensions, rather than to the microelectrophoretic mobility determined in very dilute suspensions of the coals. The influence on slurry properties of coal particle median size, BET surface area with nitrogen as adsorbate, ash content, soluble ash content, and degree of oxidation will be discussed.

Introduction: The objective of this study has been to relate the surface chemistry of a coal to its beneficiation and oxidation history in order to develop the hypothesis that coal/water slurry properties depend upon surface charge, wettability and additive adsorption from solution. Previous work[1] with four bituminous coals had suggested that, in general, particle surface charge controls slurry rheology, sedimentation stability and maximum solids content of coal/water slurries. High interparticle repulsion results in low viscosity, high solids content, poor sedimentation stability and hard-packed sediments. Low interparticle repulsion is associated with good sedimentation stability but increased viscosity and lower solids content. Incomplete wetting of a coal powder leads to hydrophobic aggregation, and decreases stability toward sedimentation. Additives may be employed to improve wetting and dispersion or to improve slurry properties by manipulating surface charge. The current work is intended to increase understanding of the contributions to slurry behavior made by the different types of materials present on heterogeneous coal surfaces.

Experimental: Properties of dry coal powders and of coal/water suspensions have been examined for six eastern bituminous coals, both freshly ground and after several months storage under air or under nitrogen. For three coals run-of-mine (ROM) samples have been compared to physically beneficiated samples. The six coals were chosen from among those surveyed as part of a large study of coal slurryability and combustion performance sponsored by the Pittsburgh Energy Technology Center of the U. S. Department of Energy.[2]

The dry powder of each coal has been characterized as to its median size, particle size distribution, B. E. T. surface area with nitrogen as adsorbate, moisture content, degree of oxidation determined by the U. S. Steel alkali extraction test[3], critical surface tension for wetting, and wettability in solutions of three surfactants[4]. The density of each coal powder in water has been determined by pycnometry and suspensions of each coal have been titrated with hydrochloric acid and sodium hydroxide solutions. For five of the six coals Gulf Research and Development Company provided surface analyses by XPS for samples recently ground under air and in some cases under nitrogen. In addition, proximate, ultimate and mineral ash analyses are available for each coal.

The microelectrophoretic mobility of each coal sample has been measured as a function of pH , in dilute potassium nitrate and in slurry supernatant, and compared to the electrophoretic mobility determined as a function of pH for 50%(wt) slurries of the coal in water, and in solutions of the nonionic surfactant Triton X-100 and of the anionic dispersant Lomar D. The apparent viscosity of the same 50%(wt) slurries was measured as a function of pH at shear rates between 2.7 and 90 s^{-1}. Apparent viscosity has also been determined as a function of coal concentration in water, at the natural pH of each coal. The sedimentation behavior of each coal has been measured as a function of pH for 25%(wt) slurries in water and as a function of coal concentration, in water and in solutions of the surfactant Triton X-100, at the natural pH of the coal. Surface tension of the slurry supernatant determined after the completion of sedimentation experiments in Triton X-100 solution is a measure of the amount of surfactant adsorbed from solution by the particles. The concentration of nine inorganic ions dissolved from the coal surface into the slurry liquor was also determined.

Results and Discussion: In Table 1 some pertinent properties of the powdered coals are compared. Except for the 6.4% ash Splash Dam coal, the median size of all samples lies between 42 and 57 µm, and in addition, these samples have similar particle size distribution widths. The Illinois *6 and Upper Freeport coals have relatively high surface areas, while the other samples have surface areas between 1.0 and 2.6 m^2g^{-1}. The results of the U.S. Steel alkali extraction oxidation test indicate that most of the coals show little sign of oxidation of the carbonaceous surface. However the 6.2% ash Lower Kittanning Coal and the Illinois *6 sample are significantly oxidized, and the aged 8.7% ash Lower Kittanning and Black Creek samples show less marked oxidation.

For samples freshly ground under air, and for samples aged under air, the pyrite content reported when proximate, ultimate, mineral ash and forms of sulfur analyses were performed is compared in Table 2 to the soluble iron content found in the liquor from 10%(wt) slurries of the coals each at its natural pH, and to the ionic strength of the same samples, as calculated

Table 1 ANALYTICAL DATA FOR COAL POWDERS

Coal	Median Size μm	Surface Area m^2g^{-1}	U.S. S. Oxidation Test % Transmission	
			Fresh	Aged
Splash Dam				
17.0% ash	43	1.3	100	96
6.4% ash	26	2.3	98	98
5.3% ash	44	1.0	92	99
1.6% ash	43	1.6	99	96
Lower Kittanning				
8.7% ash	47	2.1	92	87
6.2% ash	48	2.5	47	15
2.3% ash	42	2.6	96	95
Illinois #6				
9.7% ash	57	44.0	—	36
Black Creek				
5.8% ash	57	2.1	97	92
Upper Freeport				
21.9% ash	48	11.6	95	97
Pittsburgh Seam #8				
30.8% ash	52	2.2	100	100
6.0% ash	53	1.1	100	99

from the analyses for sodium, potassium, magnesium, calcium, iron, aluminum, silicon, chloride and sulfate ions in the slurry liquor. The reported pyrite (or pyrite plus sulfate) content is not a good indicator of either the quantity of soluble iron found or of the ionic strength of the slurry. Slurries high in soluble iron also fall in the high ionic strength group, though calcium and magnesium salts also contribute significantly to the ionic strength, particularly in the case of Pittsburgh Seam #8. In most cases, aging and oxidation appear to increase the ionic strength, but for Black Creek and Upper Freeport coals aging under air appears to decrease the solubility of the inorganic minerals present. The critical surface tension for wetting tends to be somewhat higher for high ash coals than for beneficiated coals, indicating that, as expected, the high ash coals are more hydrophilic. The Black Creek and Upper Freeport coals show marked increases in critical surface tension for wetting, again suggesting that aging under air has affected the inorganic minerals present on the surfaces of these coals.

The major result of this study is the confirmation of the hypothesis that coal/water slurry properties depend upon coal particle surface charge, as measured by electrophoretic mobility. Figure 1 shows the apparent viscosity at a shear rate of 9 s^{-1} as a function of electrophoretic mobility for two of the Splash Dam coals freshly ground under air as well as data for Illinois #6 and Hiawatha coals, as received, from our previous study[1] of four bituminous coals. High viscosity occurs at mobilities close to zero, the effect being more marked for the coals with smaller median diameter.

Table 2. PYRITE AND SOLUBLE IRON CONTENT, IONIC STRENGTH AND CRITICAL SURFACE TENSION FOR WETTING

Coal	Pyrite %(wt)	Soluble Iron mmole dm-3	Ionic Strength mmole dm-3	Critical Surface Tension for Wetting mN m-1
Splash Dam				
17.0% ash, fresh	0.11	0.003	2.3	46
17.0% ash, aged		0.007	2.4	46
6.4% ash, fresh	0.15	<0.001	1.3	41
6.4% ash, aged		<0.001	1.1	40
5.3% ash, fresh	0.04	<0.001	1.0	40
5.3% ash, aged		<0.001	3.8	40
1.6% ash, fresh	0.06	0.007	1.0	40
1.6% ash, aged		<0.001	1.0	40
Lower Kittanning				
8.7% ash, fresh	0.05	<0.001	1.1	42
8.7% ash, aged		0.100	7.1	42
6.2% ash, fresh	0.68	<0.001	1.7	42
6.2% ash, aged		<0.001	2.3	43
2.3% ash, fresh	0.08	<0.001	0.9	41
2.3% ash, aged		<0.001	1.0	41
Illinois #6				
9.7% ash, fresh	1.30	0.25	26.1	50
9.7% ash, aged		3.93	61.0	50
Black Creek				
5.8% ash, fresh	0.14	1.25	13.6	45
5.8% ash, aged		0.50	7.3	49
5.6% ash, aged and washed		0.32	1.7	..
Upper Freeport				
21.9% ash, fresh	0.35	0.66	43.6	43
21.9% ash, aged		0.43	24.5	48
Pittsburgh Seam #8				
30.8% ash, fresh	1.17	<0.001	14.6	43
30.8% ash, aged		<0.001	19.4	43
6.0% ash, fresh	0.50	<0.001	5.6	42
6.0% ash, aged		<0.001	5.0	42

When the maximum viscosity found for a coal in a 50%(wt) slurry at two different shear rates is plotted versus median size of the dry coal powder in Figure 2 it can be seen that the viscosity is markedly more dependent upon shear rate at low median size, that is, that non-Newtonian behavior is more extensive when the total surface area is high. For smaller median size effective void space can be reduced to a greater extent when flocculation occurs. The scatter of the data in Figure 2, however, indicates that the surface chemistry of a coal affects the extent of flocculation even when

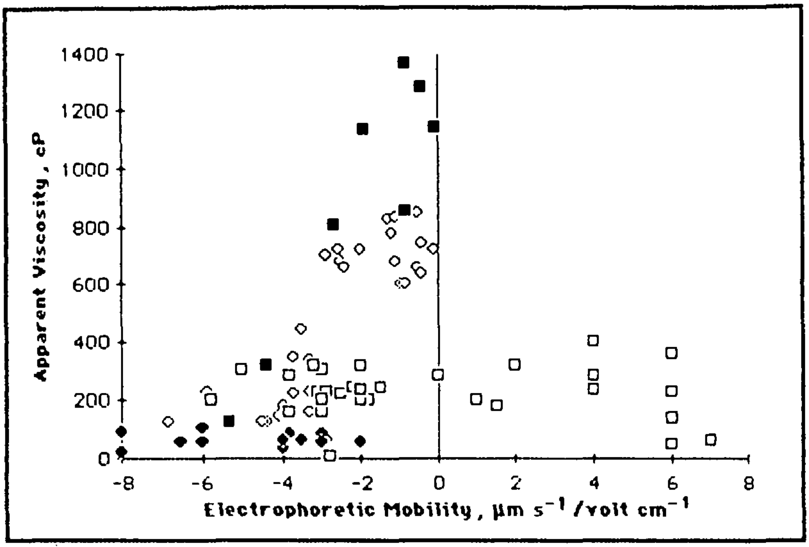

Figure 1. Apparent Viscosity as a Function of Electrophoretic Mobility at a Shear Rate of 9 s-1 for: ■ Splash Dam 6.4% ash, ● Hiawatha, ◇ Splash Dam 17% ash, □ Illinois #6

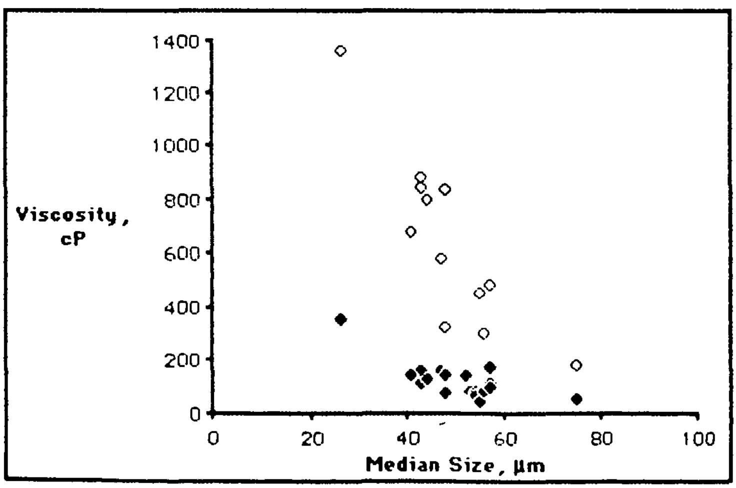

Figure 2. Maximum Viscosity as a Function of Median Size, for 50%(wt) Slurries of Sixteen Coals, at a Shear Rate of: ◇ 9 s^{-1}, ● 90 s^{-1}

particles of the same median size and size distribution width are compared. The two lowest outliers of the shear rate 9 s^{-1} curve are the two most oxidized coal samples, Lower Kittanning 6.2% ash and Hiawatha, coals which have a strongly negative mobility, and strong interparticle repulsion, over most of the pH range. On the other hand, Illinois #6, Upper Freeport and San Juan with surface areas of 44, 12 and 10 m^2g^{-1} respectively, lie on the high side of the curve, suggesting that at least a portion of the pore space is accessible to the fluid, thus decreasing the effective void space and increasing apparent viscosity for these coals.

Figure 3 demonstrates the dependence on surface charge of the median agglomerate size calculated from sedimentation data, relative to the dry particle median size. Sedimentation stability is good when there is extensive flocculation and therefore a high apparent viscosity at very low shear rates. The highly oxidized coals with low apparent viscosities show very poor stability toward sedimentation, and form hard-packed sediments, as a result of the strong interparticle repulsion. The strongly shear-thinning San Juan coal shows a high calculated agglomerate size.

In Figure 4 sedimentation rate is plotted as a function of coal concentration for three coals each at its natural pH, to demonstrate the effect of ionic strength upon stability toward sedimentation. In solutions of high ionic strength the electrical double layer is compressed towards the particle surface, decreasing interparticle repulsion and the magnitude of the electrophoretic mobility, thus promoting flocculation. As a result, sedimentation rate is decreased, and final sediment volume is increased. However at shear rates between 2.6 and 90 s^{-1} the ionic strength has little effect on the apparent viscosity measured for these slurries. This suggests that weak flocs existing at the very low shear rates occurring in sedimentation under gravity are broken apart at higher shear rates.

Figure 5 shows several patterns for the dependence of electrophoretic mobility upon pH. In Figure 5(a),(b) and (c) each pair of coals compared is similar in median particle size of the dry coal powders and in ionic strength of the slurries. In Figure 5(a) the high ash Splash Dam and Lower Kittanning samples both have a point of zero charge near pH 3, where kaolin has been reported to have a point of zero charge[5] In Figure 5(b), the low ash Splash Dam and Lower Kittanning coals are compared. Both these samples have a positive electrophoretic mobility up to at least pH 6. This appears to be the pattern of mobility associated with an unoxidized mainly carbonaceous surface. The two high ash samples of the same coals in Figure 5(a) show behavior very similar to that of the beneficiated coals at high pH, but the

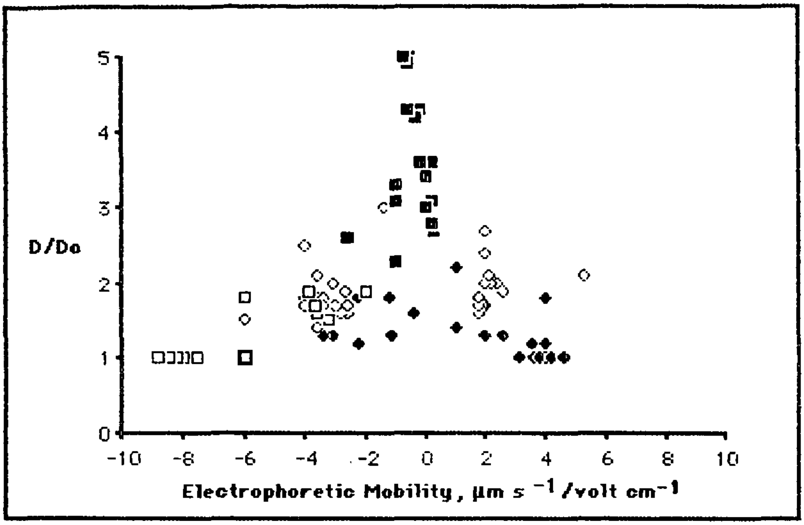

Figure #3. Ratio of Median Size D Calculated from Sedimentation Data to Median Size Do of Dry Powder, as a Function of Electrophoretic Mobility for: ◆ Pittsburgh Seam #8-3, Do = 41 µm; ■ San Juan, Do = 55 µm; ◇ Illinois #6, Do = 57 µm; □ Hiawatha, Do = 56 µm

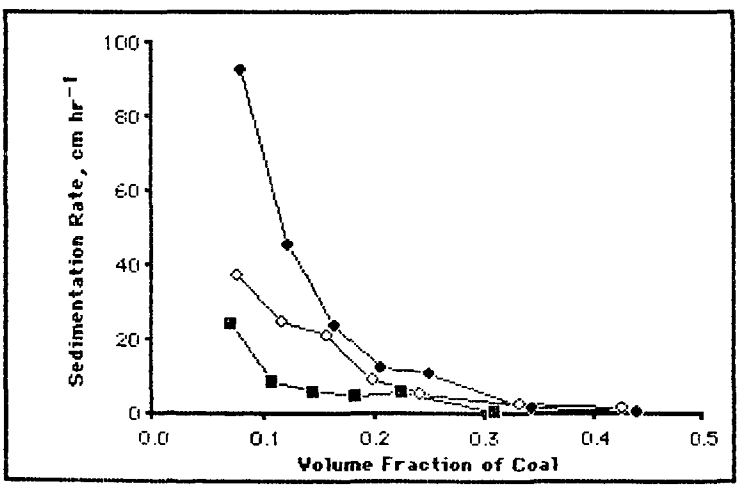

Figure 4. Sedimentation Rate as a Function of Coal Concentration for:
◆ Lower Kittanning Coal, 2.3% ash, Ionic Strength = 0.9 mmole dm^{-3}
◇ Black Creek Coal, 5.8% ash, Ionic Strength = 14 mmole dm^{-3}
■ Upper Freeport Coal, 21.9% ash, Ionic Strength = 44 mmole dm^{-3}

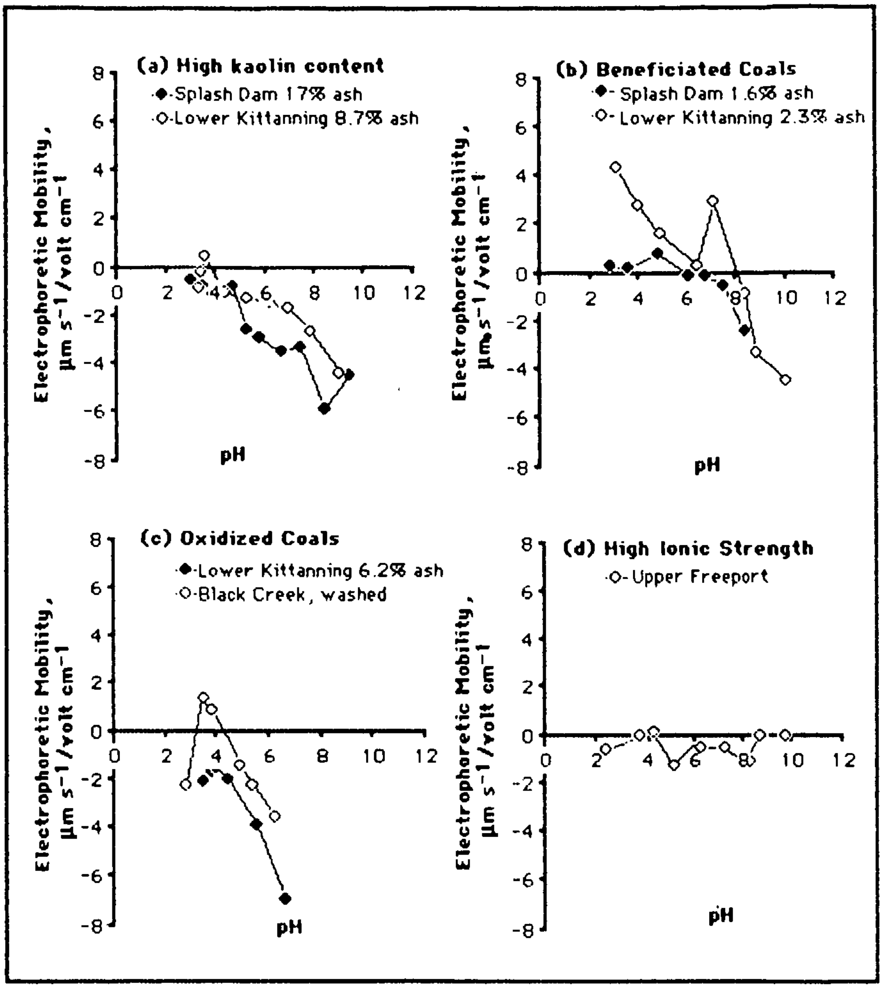

Figure 5. Electrophoretic Mobility as a Function of pH for 50%(wt) Slurries of Freshly Ground Coals, in Deionized Water

clay dominates the pattern at low pH. In Figure 5(c) the pattern for two oxidized coals is shown. Measurements could not be made above about pH 6 for either of these coals, because their slurries settled too rapidly, indicating very high interparticle repulsion and high surface charge. The patterns seen in Figure 5(b) and (c) are consistent with the observations reported by Wen and Sun[6] of electrophoretic mobility versus pH curves for very dilute suspensions of unoxidized and oxidized Pittsburgh Seam #8 vitrain. Finally Figure 5(d) shows the electrophoretic mobility observed for the high ionic strength slurries of Upper Freeport coal. The pattern for this high ash coal might be expected to resemble Figure 5(a) were it not for the high ionic strength of the slurries, which increases with pH since sodium hydroxide was added to change the slurries from their natural pH of 3. For such slurries, electrophoretic mobility is not a good predictor of the variation of viscosity with pH, though it does predict sedimentation stability and final sediment volume. High soluble iron content tends to make coal particle electrophoretic mobility less negative in the pH range from 4 to 8, but in coal/water slurries high soluble iron is usually associated with high ionic strength which decreases the absolute value of the electrophoretic mobility and makes any effects of soluble iron difficult to detect.

Conclusions: Median particle size, particle size distribution width and particle internal volume accessible to water have a strong influence upon coal/water slurry viscosity and stability. At a given median size, size distribution and surface area, slurry properties can be predicted from the electrophoretic mobility of concentrated suspensions. The effects upon surface charge, and therefore upon slurry viscosity and stability, of oxidation, beneficiation and slurry ionic strength can also be predicted, although slurry viscosity is less sensitive to ionic strength than slurry stability toward sedimentation.

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